

## Kinetic Re-Evaluation of Fuel Neutralization by AKGA

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### ABSTRACT

Baseline characterization testing previously identified alpha-ketoglutaric acid (AKGA) as a potential alternative to the current standard hydrazine (HZ) family fuel neutralization techniques in use at Kennedy Space Center (KSC). Thus far, the reagent shows promise for use in hardware decontamination operations and as a drop-in replacement for the scrubber liquor currently used in KSC four tower vapor scrubbers. Implementation of AKGA could improve process safety and reduce or eliminate generation of hydrazine-laden waste streams.

This paper focuses on evaluation of the kinetics of these decontamination reactions in solution. Pseudo first order reaction rate constants with respect to the pyridazine products (6-oxo-4,5-dihydro-1H-pyridazine-3-carboxylic acid, (PCA) and 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA)) in the presence of excess AKGA were determined by monitoring product formation using a ultra-violet visible absorption spectroscopy method. The results are presented here in comparison to previous data obtained by monitoring reactant depletion by gas chromatography with nitrogen phosphorus detector (GC-NPD).

### INTRODUCTION

The neutralization reaction between AKGA and hydrazine family fuels is being considered as an alternative chemical method for disposal of hydrazine laden waste streams generated at KSC. If applicable, this chemical neutralization method could minimize the environmental and workplace hazards associated with the containment, transport, and disposal of such waste streams. The projected cost is roughly equivalent to current disposal cost provided the product stream is found suitable for standard waste water treatment methods. Consequently, the reactions of AKGA with HZ and monomethylhydrazine (MMH) are being extensively characterized to provide data for regulatory and procedural considerations.

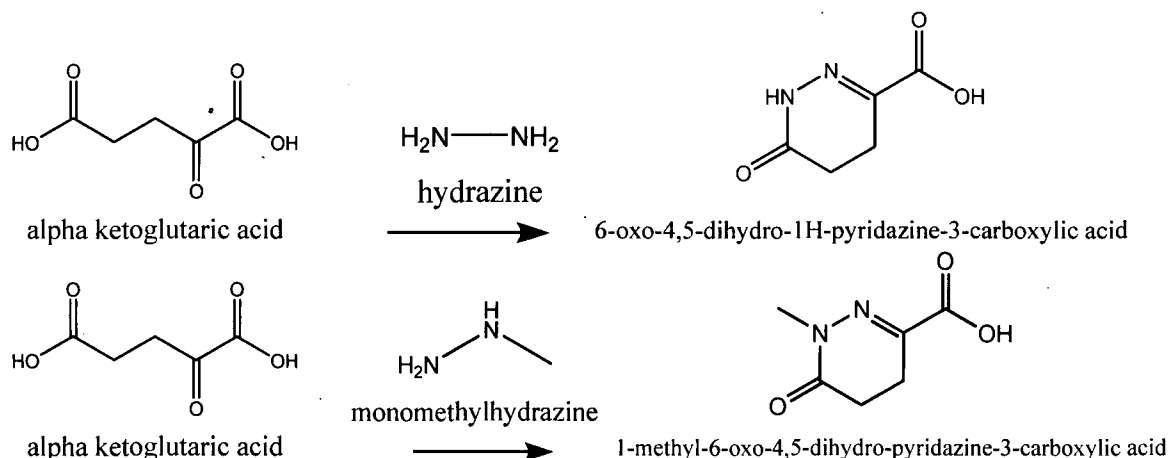
Previously reported kinetics data charted progress of the AKGA neutralization reaction by monitoring depletion of the hydrazine family fuel reactants (Hz and MMH). Derivatization methodology was used to stabilize the reactive residual fuel molecules for subsequent analysis by GC-NPD.<sup>1</sup> Given the inherent challenges associated with hydrazine analysis, a complementary approach was deemed necessary for validation. Therefore, a spectrophotometric method to monitor product formation (PCA and m-PCA) was devised. One advantage to monitoring product formation in this case is that the pyridazine products are far more stable than their hydrazine counterparts. Thus, the derivatization step and any other potential interferences are eliminated. Additionally, analysis by ultra-violet visible absorption spectroscopy (UV-Vis) is rapid as there is no need to wait for the compound of interest to elute from the column; therefore there are fewer opportunities for sample loss and degradation. The recent UV-Vis findings are presented here along with a comparison to the previously reported results.

### EXPERIMENTAL

The 1:1 reaction of AKGA with HZ or MMH yields the stabilized pyridazine products PCA (and m-PCA (respectively as follows<sup>1</sup>.

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<sup>1</sup> Only partial reactions are shown. If the reactions are 100% complete, then each also produces 2 moles of water. Other testing with Gas Chromatography – Mass Spectroscopy do not indicate any other



Pseudo first order reaction conditions were imposed to obtain the reaction rate constants with respect to the fuel reactants ( $k_{\text{HZ}}$  and  $k_{\text{MMH}}$ ). Thus, in all cases an excess of AKGA was present in the reaction mixture. The reaction rate constant  $k$ , was then determined experimentally from the slope of logarithmic plot of the increasing concentrations of the pyridazine products as measured during the first two minutes of the reaction.

The reactants were combined in a beaker with vigorous stirring. A Perkin Elmer Lambda 900 instrument was used to measure the absorbance of the reaction mixture at 280 nanometers (nm) as both PCA and m-PCA were found to exhibit strong absorbances at this wavelength. Deionized water was used as the reference. Calibration curves were constructed in a matrix of excess AKGA to mimic the reaction environment. Each reaction mixture was 650 mL on initiation. The fuel was added as an aqueous mixture to prevent "hot spot" formation and off-gassing. Discrete 1 mL aliquots were transferred from the reaction vessel to a 1 centimeter path-length quartz cuvette at approximately 20 second time intervals as the reaction progressed. Absorbance and reaction time were recorded.

## RESULTS

Figures 1 and 2 depict the graphical treatment of data for determining the reaction rate constants. Attempts to utilize data points collected prior to  $t = 60$  seconds for hydrazine and prior to  $t = 80$  seconds for MMH were unsuccessful. These data points were non-linear when plotted. This may have been the result of insufficient mixing or interference from the excess AKGA in the reaction matrix. Although the absorbances of PCA and m-PCA are much stronger than AKGA, it does exhibit a weak absorption at  $\sim 280$  nm. Consequently, the windows of initial reaction time plotted for  $k$  determination were shifted slightly to the right of what would be expected ( $t = 60$  to 210 sec for PCA and  $t = 80$  to 236 seconds for mPCA).

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substantial ( $\sim <1\%$ ) byproducts. The UV-Vis method developed in this paper only detects AKGA, PCA, and MPCA.

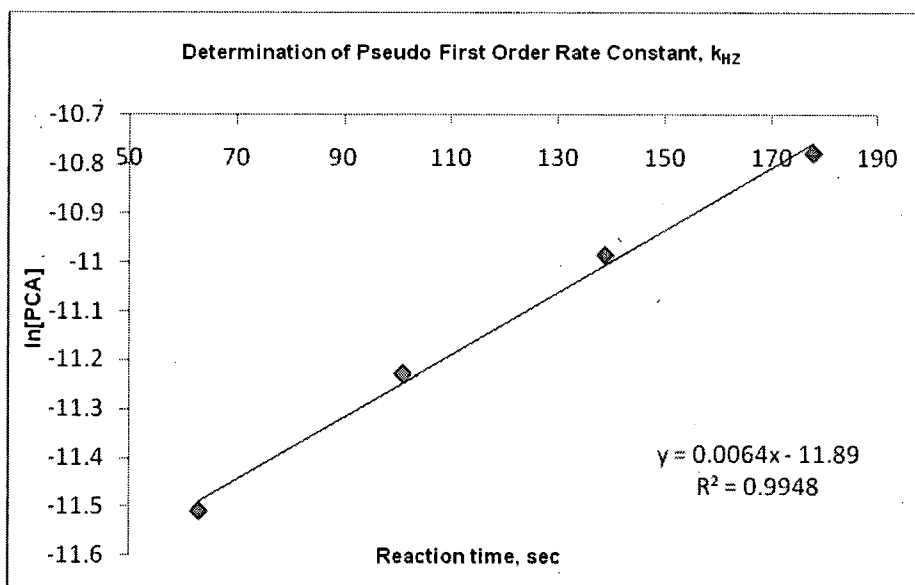


Figure 1. Graphical determination of  $k_{HZ}$  based on initial rate data.

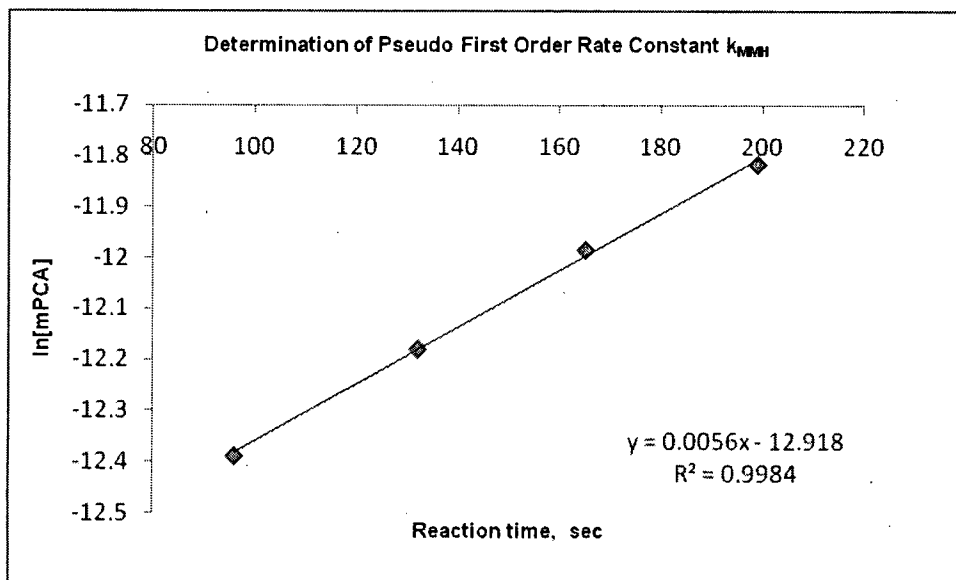


Figure 2. Graphical determination of  $k_{MMH}$  based on initial rate data.

**Table 1: Summary of data for determination of ( $k_{\text{HZ}}$ ) reaction rate constant based on PCA product formation**

| [AKGA] <sub>0</sub> , M | [HZ] <sub>0</sub> , M* | (k), sec <sup>-1</sup> | Corr. Coeff., R <sup>2</sup> | Avg. $k_{\text{HZ}}$ ** | Std Dev | % RSD |
|-------------------------|------------------------|------------------------|------------------------------|-------------------------|---------|-------|
| 0.008                   | 0.0005                 | 0.0061                 | 0.9936                       | 0.0077                  | 0.0012  | 15.85 |
| 0.008                   | 0.0005                 | 0.0064                 | 0.9948                       |                         |         |       |
| 0.008                   | 0.0005                 | 0.0080                 | 0.9743                       |                         |         |       |
| 0.007                   | 0.0005                 | 0.0087                 | 0.9945                       |                         |         |       |
| 0.008                   | 0.001                  | 0.0065                 | 0.9801                       |                         |         |       |
| 0.008                   | 0.001                  | 0.0080                 | 0.9817                       |                         |         |       |
| 0.008                   | 0.001                  | 0.0082                 | 0.9775                       |                         |         |       |
| 0.007                   | 10.001                 | 0.0095                 | 0.9626                       |                         |         |       |

\*Concentrations given in molarity (moles/L)

\*\* k values based on initial rate data recorded from t =60 to t =210 seconds

**Table 2: Summary of data for determination of ( $k_{\text{MMH}}$ ) reaction rate constant based on m-PCA product formation**

| [AKGA] <sub>0</sub> , M | [MMH] <sub>0</sub> , M* | (k), sec <sup>-1</sup> | Corr. Coeff., R <sup>2</sup> | Avg. $k_{\text{MMH}}$ ** | Std Dev | % RSD |
|-------------------------|-------------------------|------------------------|------------------------------|--------------------------|---------|-------|
| 0.006                   | 0.001                   | 0.0056                 | 0.9984                       | 0.0064                   | 0.0010  | 14.95 |
| 0.006                   | 0.001                   | 0.0050                 | 0.9818                       |                          |         |       |
| 0.006                   | 0.001                   | 0.0057                 | 0.9969                       |                          |         |       |
| 0.007                   | 0.001                   | 0.0067                 | 0.9839                       |                          |         |       |
| 0.006                   | 0.0007                  | 0.0078                 | 0.9957                       |                          |         |       |
| 0.006                   | 0.0007                  | 0.0075                 | 0.9732                       |                          |         |       |
| 0.006                   | 0.0007                  | 0.0063                 | 0.9946                       |                          |         |       |
| 0.007                   | 0.0007                  | 0.0064                 | 0.9844                       |                          |         |       |

\*Concentrations given in molarity (moles/L)

\*\* k values based on initial rate data recorded from t =80 to t =236 seconds

## CONCLUSIONS

The pseudo first order reaction rate constants  $k_{\text{HZ}}$  and  $k_{\text{MMH}}$  as determined by monitoring formation of the pyridazine reaction products PCA and m-PCA respectively are somewhat in agreement with previous data inasmuch as both methods indicate that the neutralization reactions are relatively rapid in the presence of excess AKGA. However, the k values measured by the UV-Vis method are different from those previously reported using the GC-NPD method. Specifically, the measured  $k_{\text{HZ}}$  by UV-Vis is 0.0077 sec<sup>-1</sup> is much higher compared to 0.0011 sec<sup>-1</sup> as measured by the GC-NPD method. The  $k_{\text{MMH}}$  as measured by UV-Vis method is 0.0064 sec<sup>-1</sup> is more comparable to results from the GC-NPD method at was 0.0053 sec<sup>-1</sup>. We believe the large differences between  $k_{\text{HZ}}$  for the two different measurement methods are due to the length of time required for the reactants to elute from column in the GC-NPD method (~ 9 minutes) allowing more time for interference from the derivatization process required for the GC-NPD method. Meanwhile, m-PCA eluted from the column in only about two minutes thus minimizing time for forming interferences.

The spectrophotometric method of monitoring the pyridazine products should be considered a more accurate quantitation of reaction rate for several reasons. For one, the pyridazine products (PCA and m-PCA) are far more stable than the corresponding fuel reactants. No derivatization is required and values are not subject to sample loss and discrepancy due to reaction, degradation, or adsorption of the MMH and HZ reactant molecules. In addition, spectrophotometric analysis is complete in several seconds whereas the GC-NPD analysis requires several minutes for detection. In a reaction rate measurement scenario this analysis time can introduce significant error into the measurement. Moreover, there are opportunities for sample loss and degradation at the injector as well as decreased sensitivity arising from column degradation when using the GC method. Such systematic errors are circumvented by measuring the absorbance of the reaction mixture directly. Therefore, the pseudo first order reaction rate constants reported here should be considered more accurate than those previously reported.

## REFERENCES

1. Oropeza, C., Kosiba, M., and Davis, C. "Preliminary Characterization of Alternative Hydrazine and Monomethylhydrazine Neutralization Reactions." JANNAP Propulsion and Subcommittee Meeting, Las Vegas, Nevada, April 2009b.